SYNOPSIS

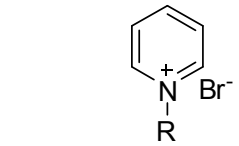
(1) TITLE OF THE SYNOPSIS

"STUDY OF MICELLAR CHARACTERISTICS OF SOME CATIONIC SURFACTANTS BY CONDUCTIVITY, SURFACE TENSION AND FLUORESCENCE MEASUREMENTS"

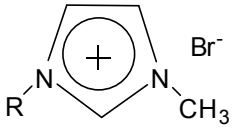
(2) INTRODUCTION

The physicochemical and interfacial properties of surfactants are fascinating and crucial for understanding their role as well as their use in pharmaceutical, industrial and biological fields [1-3]. Micelle formation and interfacial adsorption behavior of the surfactants depend on molecular structure and on various environmental factors, e.g. temperature, pH and presence of additives etc. Recently, surfactants have shown to be of great interest in scientific and industrial application due to their solubilization, suspension, dispersion and transportation ability [4-7]. Variety of conventional and novel cationic surfactants ranging from monomeric to dimeric with different heterocyclic head groups (**Scheme-I**) have been synthesized (pyridinium, imidazolium and quinolinium) for various applications [8-9]. Studies based on pyridinium salts enabled synthesis of quinolinium based cationic surfactants that are believed to have wide applications including antimicrobial activity [10-11]. Quinolinium and isoquinolinium salts represent important synthetic building blocks, which can be generated by alkylation or acylation of quinoline and isoquinoline. Addition of nucleophilic reagents to these salts proved to be a useful method for the synthesis of substituted quinoline and isoquinoline derivatives [12]. Other interesting applications of quaternary pyridinium and quinolinium salts are their use in analytical and physical research, disinfectants in various technological applications and cosmetic

products etc. [13]. Pyridinium and imidazolium quaternary compounds are competitive inhibitors of acteylcholinesterase [14] and are used as micellar catalysts for decomposition of toxic esters [15].



Alkylpyridinium bromide



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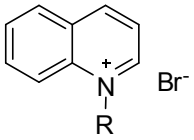
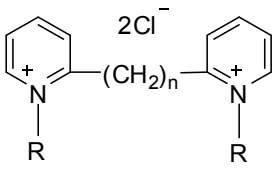


N-alkylquinolinium bromide



Pyridinium gemini surfactant

R = decyl, dodecyl, tetradecyl, hexadecyl, octadecyl

Scheme I. Structure of some novel cationic surfactants

Gemini surfactants possess a structure resembling a pair of conventional single chain surfactants covalently connected by a spacer. The spacer can vary in length and chemical structure. The study of gemini surfactants has generated much interest due to their unusual solution and interfacial properties and their enhanced performance in applications compared to analogous single chain surfactants [16-17].

Surfactants tend to form micelle in aqueous solutions at a characteristic concentration named critical micellar concentration (cmc). It is a key parameter in surfactant screening and usually to compare the effects of different surfactants makes sense only when concentration is above their cmc. A variety of methods

viz. surface tension, electrical conductivity, calorimetry, UV absorption spectroscopy and dynamic light scattering etc. have been used for the determination of cmc. Fluorescence based methods have also been used for the determination of cmc and micellar aggregation number. Since fluorescence spectroscopy is quite more sensitive than optical absorption , the design of new fluorescence probe molecules is a subject of intense research [18-19].

To assess the basics of a surfactant, study of micellization process is essential. Much work has been done on the conventional and commercially available surfactants. However systematic studies related to micellar characteristics of novel monomeric and gemini surfactants like pyridinium, quinolinium are limited. Therefore, in the present investigation thorough studies regarding physicochemical properties of the micellar and interfacial adsorption behavior such as thermodynamics of micellar formation, counterion binding, surface excess, microenvironment will be undertaken for some conventional cationic monomeric, gemini, pyridinium and quinolinium based surfactants. An attempt will also be made to study their solubilization property and catalyzing functions. An efficient technology will be developed for the determination of some polycyclic aromatic hydrocarbons contaminated in the soil and ground water.

(3) REVIEW OF THE EARLIER WORK

In view of important uses and applications of surfactants, detailed fundamental studies of the existing and newer amphiphilic systems are in progress. Presently there is a great interest to understand the physicochemical aspects of cationic surfactants in view of their applications in biological, pharmaceutical and environmental fields which help to select the most suitable surfactants with desired surface activity. During the past few years, Ghosh and his group have been

carrying out the physicochemical and thermodynamic properties of some monomeric and gemini surfactants [20-22]. The role of these surfactants as micellar catalyst for various nucleophilic reactions [23-24] has also been studied. Mixture of different surfactant often favorably interact in the formation of mixed micelles and exhibit superior behavior or synergism in their effects on various micellar properties of a system.

Extensive studies on the micellar characteristics of conventional monomeric surfactants have been done [25-29] but little is known about novel surfactants like pyridinium based gemini, quinolinium and imidazolium surfactants [30-32]. Recently Kuca et al. [33] synthesized quinoline cationic surface active agents differing in the length of the side alkyl chains (C_8 to C_{20}). Quagliotto et al. [34] synthesized a novel series of gemini surfactants by quaternization of the 2, 2'- (α-ώ alkanediyl) bis pyridines with N-alkylating agents bearing the pyridinium ring as the head group. They have also studied the synthesis and properties of methyl substituted quinolinium cationic surfactants [35].

Gemini surfactants with quaternary ammonium bromide head groups having linear alkyl tails have been studied by Zana et al. [36-37]. Kabir-ud-Din and coworkers studied the surface properties and mixed micellization of cationic gemini surfactants with ethylene amines as well as with conventional surfactants in aqueous media [38]. Mixtures of various monomeric and dimeric surfactants using conductivity and fluorescence measurements in single and mixed systems have been investigated by Moya and research group [39]. They have also explored kinetic studies in mixed surfactant systems [40]. Emilia et al. investigated micellar and surface properties of variety of gemini and conventional surfactants [41].

Surfactant systems can be applicable for the removal of residual organics from contaminated aquifers through the process like micellar solubilization. The presence of toxic organic pollutants like naphthalene, anthracene, phenanthrene and so on in the soil matrix constitutes a long term source of groundwater contamination, due to their low solubility in water [42-43]. The solubility efficiency in gemini cationic surfactant micelles and their comparison with conventional surfactants has been discussed by Menger et al. [44]. Huang and coworkers documented solubilization of phenanthrene in gemini surfactants [45]. Zhu et al. studied solubilicity of aromatic hydrocarbons in mixed surfactants systems [46]. A systematic study may be conducted for further understanding of how solubilization occurs in these novel surfactant systems.

(4) OBJECTICVES OF THE STUDY

The specific objectives of the present investigation are:

(i) To study the physicochemical characteristics of some conventional and novel cationic monomeric, pyridinium, quinolinium and gemini surfactants by conductometric, surface tension and fluorescent measurements.

(ii) To study the thermodynamics of micellization.

(iii) To study the effect of addition of solvents on micellization.

(iv) To analyze the surfactant solubilization characteristics viz., molar solubilization ratio, micelle-water partition coefficient and free energy of solubilization etc. for polycyclic aromatic hydrocarbons.

(v) To study the effect of surfactants on the kinetics of nucleophilic substitution reactions.

(5) NOTEWORTHY CONTRIBUTIONS

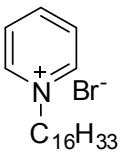
Significant uses and application of surfactants in various fields, demand their detailed micellar characteristics and energetics of micelle formation. Changes of the molecular structure of surfactants have important consequences for the micellar characteristics of their solutions, and hence an application of the organized assemblies formed. Heterocyclic compounds like quinolinium and pyridinium derivatives have received considerable attention due to their pharmacological properties. These compounds have numerous applications in various branches of industry and research. One of the promising technologies is the use of surfactants to mobilize and solubilize many environmental pollutants like polycyclic aromatic hydrocarbons from the surface and subsurface contamination.

(6) PROPOSED METHODOLOGY DURING THE TENURE OF THE RESEARCH WORK

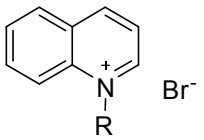
The entire experimental work will be done in the following steps:

I. Micellar Characteristics of Some Pyridinium, Quinolinium and Cationic Gemini Surfactants

Synthesis of quinolinium and pyridinium based cationic surfactants (**Scheme-II**) will be done in collaboration with Dr. Kamil Kuca (Center of Advanced Studies and Department of Toxicology, Faculty of Military Health Sciences, Czech Republic).



Cetylpyridinium bromide



$R = C_nH_{2n+1}$

N-alkylquinolinium bromide

Scheme-II. Structures of pyridinium and quinolinium cationic surfactants

The critical micelle concentration, degree of counter ion binding, and interfacial parameters of some quinolinium and pyridinium based surfactants will be determined using conductometric and surface tension measurements. Micellization of conventional and gemini surfactant will also be studied for comparison.

II. Study of Micellar Properties by Fluorescence Spectroscopy

Critical micelle concentration and other micellar properties will be studied by spectrofluorimetric technique. The fluorescence probe technique is becoming increasingly popular in the study of surfactant adsorption, polymer surfactant interactions and microemulsion etc. This method involves the use of a hydrophobic fluorescence dye which exhibits different fluorescence characteristics depending upon the properties of the solubilizing medium. Values of surfactant cmc are determined from changes in fluorescence spectra or intensities upon micelle formation.

III. Thermodynamics of Micelle Formation of Surfactants

Micellar properties of surfactants are significantly influenced by the temperature. In combination with structural data, knowledge of thermodynamics

could lead to a more complete understanding of micelle dynamics. Temperature effects on micellar and surface properties of surfactants will be studied in the presence of additives. Various thermodynamic parameters viz. standard free energy (ΔG°_m), entropy (ΔS°_m) and enthalpy (ΔH°_m) of micellization will be obtained for monomeric and gemini surfactant systems.

IV. Effect of Addition of Organic solvents on Micellization

The role of cosolvents in the micellization process is of considerable interest both from the fundamental and applied view points since applications of surfactants in many physicochemical and interfacial phenomenon largely depend on it. An attempt will be made to study the micellization of some surfactants in water-organic solvent mixed media (ethylene glycol, 1,4-dioxane, ethanol, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran etc.) by means of conductivity and surface tension measurements.

V. Water Solubility Enhancements of PAHs by Surfactants

Micellar solubilization is an important step for removal of organic contaminants from the soil matrix, especially for low aqueous solubility of organic contaminants. The contamination of soil and water by polycyclic aromatic hydrocarbons is a widespread environmental concern. Water solubility enhancement of some PAHs i.e. naphthalene and anthracene etc. using novel micellar solutions will be studied. A molar solubilization ratio (MSR) is given to quantify the effectiveness of a surfactant in solubilizing a given solubilizate. It can be defined as the number of organic compound solubilized per moles of surfactant added to the solution and can be calculated as per eq. (1)

$$MSR=(S-S_{cmc})/(C_s-CMC) \quad (1)$$

Where,

S = Apparent solubility of organic compound at surfactant concentration Cs (C_s>CMC).

S_{cmc}= Apparent solubility of organic compound at CMC.

Furthermore analysis of the other solubilization characteristics viz. micelle-water partition coefficient, free energy of solubilization and binding constant would be valuable in evaluation of the solubilization capacity of surfactants.

VI. Nucleophilic Substitution Reactions in pure and mixed micellar systems

Esterolysis of carboxylate, phosphate and sulphonate esters will be studied in micellar media by spectrophotometric measurements. Effect of solvents on micellar kinetics with gemini and conventional cationic surfactants will be monitored. Kinetic studies in cationic/gemini mixed micellar systems will also be investigated.

(7) EXPECTED OUTCOME OF THE PROPOSED WORK

The micellar behavior of the novel surfactants would be very useful to achieve a better insight into their interactions. Studies on the physicochemical characterization of single and mixed novel cationic surfactants usually yield necessary information to optimize and design surfactant systems with the desired properties. The present study may be useful for the selection of mixed micellar systems and prediction of their micellar stability. Thermodynamics of micelle formation is essential to better understand how to develop stable micelles for use

in pharmaceutical and industrial applications. Studies on micellar solubilization can be used to minimize the environmental pollution caused by toxic organic compounds.

(8) BIBLIOGRAPHY IN STANDARD FORMAT

1. N. Sardar, M. Kamil, Kabir-ud-Din, *Ind. Eng. Chem. Res.,* 2012, **51**, 1227.
2. A. Rodriguez, M. M. Graciani, M. Vargas, M. L. Moya, *J. Phys. Chem. B,* 2008, **112**, 11942.
3. Y. Moroi, Micelle Theoretical and Applied Aspects, Plenum Press, New York, 1992.
4. A. Mohr, P. Talbiersky, H. G. Korth, R. Sustmann, R. Boese, D. Blaser, H. Rehage, *J. Phys. Chem. B*, 2007, **111**, 12985.
5. Y. S. S. Sadovskii, T. N. Solomoichenko, M. K. Turovskaya, I. V. Kapitanov, Z. P. Piskunova, M. L. Kostrikin, T. M. Prokopeva, A. F. Popov, *Theoretical and Experimental Chemistry*, 2012, **48**, 122.
6. H. Naorem, S. D. Devi, *J. Surface. Sci. Technol.*, 2006, **22**, 89.
7. J. Mata, J. Patel, N. Jain, G. Ghosh, P. Bahadur, *J. Colloid Interf. Sci.,* 2006, **297**, 797.
8. G. Liu, D. Gu, H. Liu, W. Ding, Z. Li, *J. Colloid Interf. Sci.*, 2011, **358**, 521.
9. G. Viscardi, P. Quagliotto, C. Barolo, P. Savarino, E. Barni, E. Fisicaro, *J. Org. Chem,*. 2000, **65***,* 8197.
10. J. R. Harjani, R. D. Singer, M. T. Garcia, P. J. Scammells, *Green Chem*., 2008, **10**, 436.
11. M. Joshaghani, E. Rafiee, F. Shahbazi, H. Jafari, S. Amiri, M. Omidi, *Arkivov*, 2007, **1**, 164.
12. F. M. Moghaddam, H. Saeidian, M. Kiamehr, Z. Mirjafary, S. Taheri,

Arkivoc, 2010, **11**, 91.

13. R. K. Mahajan, S. Mahajan, A. Bhadani, S. Singh, *J. Phys. Chem. Chem. Phys.,* 2012, **14**, 887.
14. R. S. Martin, J. M. Campos, A. C. Garcia, O. C. Lopez, M. B. Coronel, A. R. Gonzalez, M. A. Gallo, J. C. Lacal, A. Espinosa, *J. Med. Chem.,* 2005, **48***,* 3354.
15. N. Singh, K. K. Ghosh, *Indian J. Chem., Sec B,* 2012, **51**, 611.
16. H. Akbas, M. Boz, C. Batigoc, *Spectrochimica Acta Part A*, 2010, **75**, 671.
17. A. K. Tiwari, M. Sowmiya, Sonu, S. K. Saha, *J. Mol. Liquids*, 2012, doi:10.1016/j.molliq.2011.12.004.
18. A. P. Romani, A. E. H. Machado, N. Hioka, D. Severino, M. S. Baptisa, L. Codognoto, M. R. Rodrigues, H. P. M. de Oliveria, *J. Fluoresc*., 2009, **19**, 327.
19. M. Sowmiya, A. K. Tiwari, S. K. Saha, *J. Colloid Interf. Sci.,* 2010, **344**, 97.
20. S. K. Verma, K. K. Ghosh, *J. Surfact. Deterg.*, 2011, **14**, 347.
21. S. Kolay, K. K. Ghosh, A. C. J. Moulins, R. M. Palepu, *J. Solution Chem.,* 2008, **37**, 59.
22. D. Tikariha, N. Singh, M. L. Satnami, K. K. Ghosh, N. Barbero P. Quagliotto, *Colloids Surf. A: Physicochem. Eng. Aspects,* 2012, doi.org/10.1016/j.colsurfa.2012.06.032.
23. N. Singh, K. K. Ghosh, K. Kuca, J. Marek, *Int. J. Chem. Kinet*., 2011, **43,** 569.
24. B. Kumar, M. L. Satnami, K. K. Ghosh, K. Kuca, *J. Phys. Org. Chem*., 2012, 9999.
25. S. Zhao, H. Zhu, X. Li, Z. Hua, D. Cao, *J. Colloid Interf. Sci.*, 2010, **350**, 480.

26. G. P. Jones, S. Regismond, K. Kwetkat, R. Zana, *J. Colloid Interf. Sci.*, 2001, **243**, 496.
27. P. B. S. Junior, V. A. O. Tiera, M. J. Tiera, *Ecl. Quim*., 2007, **32**, 47.
28. A. Adak, A. Pal, M. Bandyopadhyay,. *Indian. J. Chem. Technol*., 2005, **12**, 145.
29. D. Velluto, C. Gasbarri, G. Angelini, A. Fontana, *J. Phys. Chem. B.*, 2011, **115**, 8130.
30. V. I. Martin, A. Rodriguez, M. M. Graciani, M. L. Moya, *J. Colloid Interf. Sci.*, 2012, **368**, 326.
31. G. Chigwada, D. Wang, C. A. Wilkie, *Polym. Degrad. Stab*., 2006, **91**, 848.
32. P. D. Galgano, O. A. E. Seoud, *J. Colloid Interf. Sci.,* 2010, **345**, 1.
33. J. Marek, V. Buchta, O. Soukup, P. Stodulka, J. Cabal, K. K. Ghosh, M. Musilek, K. Kuka, *Molecules,* 2012, **17**, 6386.
34. P. Quagliotto, C. Barolo, N. Barbero, E. Barni, C. Compari, E. Fisicaro, G. Viscardi, *Eur. J. Org. Chem.,* 2009, 3167.
35. P. Quagliotto, N. Barbero, C. Barolo, E. Artuso, C. Compari, E. Fisicaro, G. Viscardi, *J. Colloid Interf. Sci.*, 2009, **340***,* 269.
36. M. In, R. Zana, *J. Dispers. Sci. Technol.*, 2007, **28**, 143.
37. R. Zana, *J. Colloid Interf. Sci.*, 2002, **248**, 203.
38. Kabir-ud-Din, P. A. Koya, *J. Chem. Eng. Data*, 2010, **55**, 1921.
39. A. Rodriguez, M. M Graciani, M. Angluo, M. L. Moya, *Langmuir,* 2008, **24**, 12785.
40. M. M. Graciani, A. Rodriguez, M. L. Moya, *J. Colloid Interf. Sci.,* 2008, **328**, 324.
41. E. Igleasias, J. Phys. Chem. B., 2001,**105**, 10287.

42. S. Paria and P. K. Yuet, *Ind. Eng. Chem. Res.*, 2006, **45,** 3552.

43. A. A. Dar, G. M. Rather, A. R. Das, *J. Phys. Chem. B.*, 2007, **111**, 3122.

44. K. Gharanjig, M. S. Kiakhani, A. R. T. Bagha, A. Khosravi, F. M. Menger, *J. Surfact. Deterg.*, 2011, **14**, 381.

45. J. Wei, G. Huang, H. Yu, C. An, *J. Chem. Eng.*, 2011, **168**, 201.

46. L. Zhu, S. Feng, *Chemosphere,* 2003, **53**, 459.

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